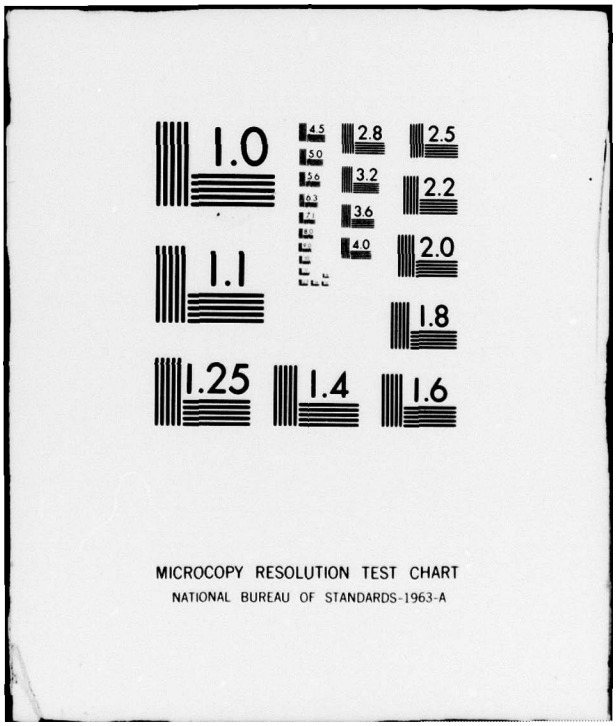
AD-A080 016 ARMY MEDICAL BIOENGINEERING RESEARCH AND DEVELOPMENT --ETC F/G 7/3
EVALUATION OF OZONE OXIDATION AND UV DEGRADATION OF DIMETHYLNIT--ETC(U)
DEC 79 E A KOBYLINSKI, B W PETERMAN

UNCLASSIFIED USAMBRDL-TR-7908 NL

| OF |
AD-
A080016

END
DATE
FILMED
2-80
DDC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD

LEVEL II

TECHNICAL REPORT 7908

EVALUATION OF OZONE OXIDATION AND UV DEGRADATION OF DIMETHYLNITROSAMINE

EDMUND A. KOBYLINSKI, 1LT, MSC
BARRY W. PETERMAN, CPT, MSC

US ARMY MEDICAL BIOENGINEERING RESEARCH and DEVELOPMENT LABORATORY
Fort Detrick
Frederick, Md. 21701

DECEMBER 1979

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

US ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
FORT DETRICK
FREDERICK, MD 21701

NOTICE

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: TECHNICAL REPORT 7908
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER: 9
4. TITLE (and Subtitle): 6 EVALUATION OF OZONE OXIDATION AND UV DEGRADATION OF DIMETHYLNITROSAMINE.
5. TYPE OF REPORT & PERIOD COVERED: Technical Report. Sep [illegible] - Nov [illegible]79,
6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): 10 EDMUND A. KOBYLINSKI, 1LT, MSC; BARRY W. PETERMAN, CPT, MSC
8. CONTRACT OR GRANT NUMBER(s): 12 18
9. PERFORMING ORGANIZATION NAME AND ADDRESS: US Army Medical Bioengineering Research & Development Laboratory, ATTN: SGRD-UBG, Fort Detrick, Frederick, MD 21701
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 62720A; 14 3E162720A835/00/137
11. CONTROLLING OFFICE NAME AND ADDRESS: US Army Medical Research & Development Command, ATTN: SGRD-AJ, Fort Detrick, Frederick, MD 21701
12. REPORT DATE: December [illegible]79 (11) (17 Ø Ø)
13. NUMBER OF PAGES: 16
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): 14 USAMBRDL-TR-7908
15. SECURITY CLASS. (of this report): UNCLASSIFIED
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Batch
Completely mixed
Dimethylnitrosamine
First-order reaction
Ozone
Ultraviolet light

Accession For
NTIS GRA&I
DDC TAB
Unannounced
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or special
A | 1 0.02 MIN

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Dimethylnitrosamine was detected in the wastewater leaving Holston Army Ammunition Plant. The wastewater from the ammonia stripping column was treated with (1) ozone, (2) ultraviolet light and (3) a combination of both ozone and ultraviolet light. Ozone alone does not degrade DMN. Ultraviolet degrades DMN yielding first-order kinetics with a rate constant of 0.025 min^{-1}. A special run using UV was performed on the feed to the ammonia stripping column and it also yielded first-order kinetics with a rate constant of 0.044 min^{-1}.

1 0.044 MIN

JOB

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

407 838

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The identification of 1,1-dimethylnitrosamine (DMN) in a wastewater stream leaving the Holston Army Ammunition Plant (HAAP), was reported in a January 1979 progress report from Midwest Research Institute (MRI) to the US Army Medical Bioengineering Research and Development Laboratory (USAMBRDL). MRI reported finding DMN in grab samples taken from three locations at HAAP.

The wastewater stream containing DMN was generated from the blowdown of an ammonia recovery distillation column housed in Building A-1. Feedwater for this operation is a wastewater generated during production of RDX. The production wastewater is collected and stored prior to ammonia recovery processing. When the storage tank is filled, (approximately 6 months are required for filling the tank at current production levels) the distillation column is put into operation. Approximately 4 to 5 days of continuous column operation are required to empty the storage tank. The blowdown from the column is discharged to a drainage ditch which eventually discharges to Arnott Branch, a feeder stream to the Holston River.

The samples for the Midwest Research Institute study were collected from the bottom of the distillation column (still bottoms) and at two sites on the Arnott Branch. The first branch site was located 40 feet downstream from the junction of the drainage ditch and the Arnott Branch. The second site was 500 feet downstream from the branch and ditch junction. The concentration of DMN contained in the one quart grab samples collected at these sites are shown in Table 1.[1]

TABLE 1. DIMETHYLNITROSAMINE CONCENTRATION (mg/l)

Site 1		Site 2		Site 3	
Day 1	Day 3	Day 1	Day 3	Day 1	Day 3
500 (one analysis)	500 (one analysis)	0.87±0.03 (two analyses)	1.6±0.1 (two analyses)	6.2±1.0 (four analyses)	11.6 (one analysis)

Results of the MRI findings were sent to the US Army Environmental Hygiene Agency (USAEHA) where the problem could receive additional attention. In February of 1979, USAEHA conducted a comprehensive sampling of HAAP wastewaters to determine concentration of DMN in the wastestream. USAEHA personnel collected samples at the same sites as MRI. Additionally, distillation column feedwater was sampled.

Grab samples taken, by USAEHA, of the distillation column feedwater contained DMN concentrations ranging from 7 to 18 mg/l with a mean of 12 mg/l.[2] The DMN concentration in the grab samples collected from the still bottoms also ranged from 7 to 18 mg/l with a mean of 14 mg/l. Seven samples were taken from the feed and 10 taken from the still bottoms. There was no significant difference between the feed and bottoms. Results of the USAEHA samples collected 500 feet from the junction of Arnott Branch and the ditch, showed DMN concentration of 0.036 mg/l.

This study was conducted on-site at HAAP during the period from 12 to 14 September 1979. USAEHA analyzed the sample for DMN by using GC and GC/MS.

OBJECTIVE

The objective of this study was to provide information on the feasibility of using ozone (O_3), ultraviolet light catalyzed ozone (UV/O_3), and ultraviolet light (UV) treatment for removal of DMN from a waste stream.

EXPERIMENTAL

General

Oxidation of organic compounds with ozone is a relatively new process in wastewater treatment. Ozone has the ability to reduce the total organic carbon (TOC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of wastewater streams. Organic compounds can be oxidized, to CO_2 and H_2O, while nitrogen can be oxidized to NO_3^-.[3] McCarthy *et al.*[4] have shown that TOC can be removed by total oxidation. TOC removal rates increase at high pH values.[5-7] The rate of TOC removal is dependent on the availability of ozone, which is itself dependent on the rate of mass transfer of O_3 from the gas phase to the liquid media. Ultraviolet light is often used as a catalyst to increase ozonation efficiency.[8]

Photolysis is another method that may be used to degrade chemical compounds. In this process, the compound absorbs the radiation and becomes energized. The excited compound may be transformed to a diradical and degrade. The rate of degradation is dependent on the wavelength of the radiation and the intensity of the radiation. Ultraviolet lamps produce a light which is more intense than UV light in ordinary sunlight and therefore may be effective in waste treatment.[9]

Materials

Substrate. Wastewater samples containing DMN were collected from the distillation column blowdown discharge, for seven of the eight experiments. Distillation column feed was used for one experiment.

Reactor. The stainless steel reactor column (Fig. 1), is 6.6 inches in diameter, is 78 inches tall, resulting in a cross sectional area of 31.4 in^2 and a reactor volume of 2449.2 in^3. A sintered stainless steel gas sparger, having a mean pore size of 5 microns, is located approximately 2 inches above the base of the reactor. A 34-watt UV lamp running vertically through the center of the column, emits light at a wavelength of 253.7 nm.

The reactor is capable of batch or continuous operation. With gas flow rates of 20 SCFH and above, the reactor contents are completely mixed.[4]

Approach

General. A schedule for the experimental treatments is presented in Table 2. Prior to the start of a run, 30 liters of wastewater were pumped into the reactor. A time = 0 sample was collected from the reactor before initiating treatment. Each experimental run was 2 hours in duration with reactor samples collected at 15 minute intervals. All experiments were conducted in batch mode.

TABLE 2. SCHEDULE OF EXPERIMENTAL TREATMENTS

Run No.	Day	Time	Treatment
1	12 Sep	1340-1540	Air stripping only
2	13 Sep	0850-1050	Ozone
3	13 Sep	1120-1320	Ultraviolet light
4	13 Sep	1350-1550	Ultraviolet light - ozone
5	14 Sep	0835-1035	Ultraviolet light - ozone
6	14 Sep	1100-1300	Ultraviolet light
7	14 Sep	1340-1540	Ultraviolet light[a]

a. Feed material was the wastewater entering Building A-1.

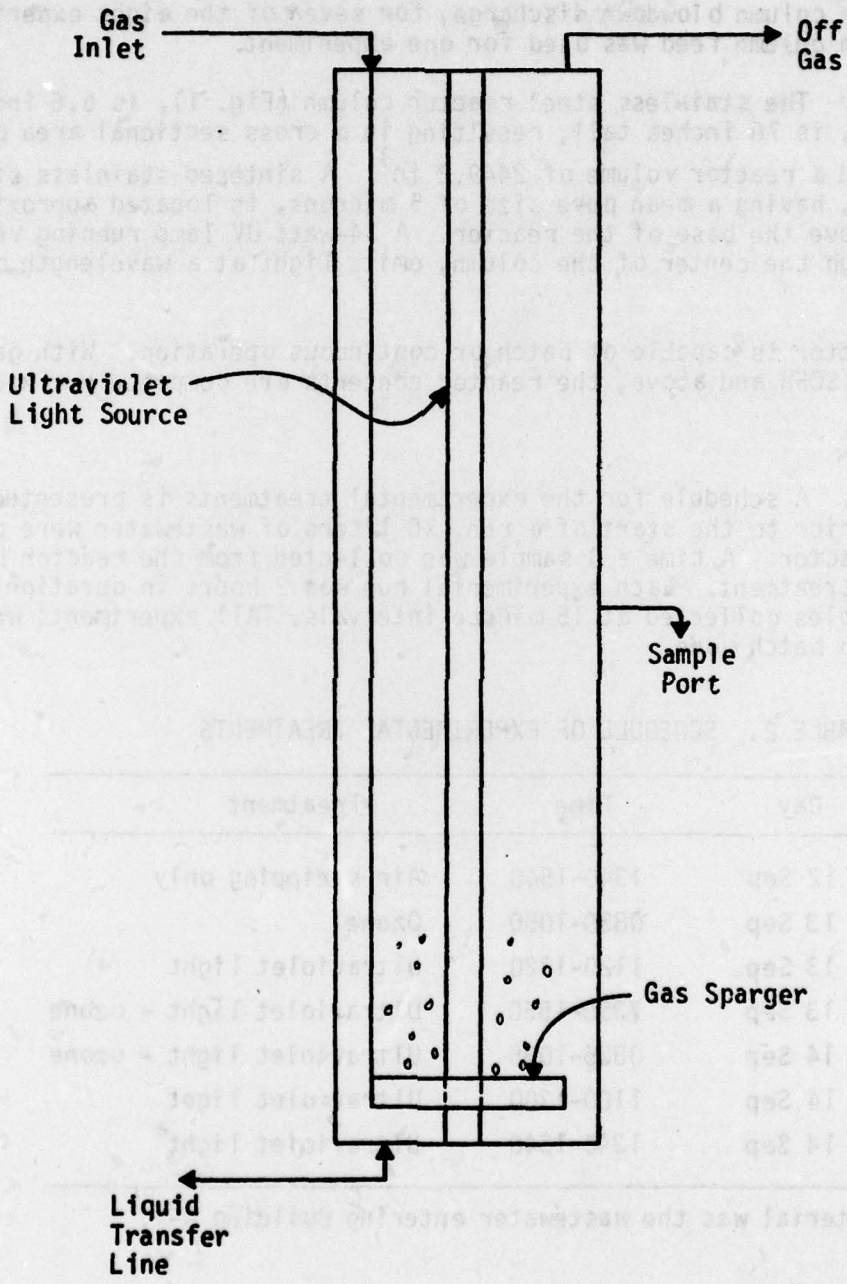


Figure 1. Reactor Schematic.

Experimental Treatments

The stripping experiment (run #1) was conducted by bubbling dry compressed air at 10 psig and 20 SCFH through the reactor. The purpose of this experiment was to evaluate the volatility of DMN.

Ozone oxidation (run #2) was carried out by bubbling an air/ozone mixture containing approximately 1 weight percent ozone through the reactor at 10 psig and 20 SCFH.

During the UV experiments (runs #3 and 6) air, again at 10 psig and 20 SCFH, was bubbled through the column to maintain mixing during the treatment.

UV catalyzed ozone oxidation (runs #4 and 5) was carried out under the same conditions as oxidation with ozone above, with the only difference being the presence of the UV light source.

The final experiment (run #7) was performed using the distillation column feedwater as a substrate. During this experiment no air was introduced into the column. Mixing was maintained by recirculating the wastewater through the column.

Sampling and Analysis. At the time of sample collection during each experimental run, wastewater temperature and pH were recorded. All samples were collected in amber jars with teflon lined caps and then placed in a box to eliminate exposure to sunlight. Laboratory analyses of all samples for DMN concentration were performed at USAEHA utilizing gas chromatography and mass spectrometry.

RESULTS

Data presented in Table 3 shows that the DMN concentration in the wastewater was not reduced by treatment with ozone. Fotchman and Eisenberg,[10] and Perry et al.,[11] reported similar results using an aqueous solution of DMN.

Limited destruction of DMN was noticed (Table 4 and Figure 2) when the wastewater was treated with ozone in the presence of UV light.

The data in Table 5 and Figure 3 show that UV light was an effective method for reducing the DMN concentration and that the rate of reduction of DMN was first order. A rate constant of 0.025 min^{-1} was computed using least squares. The determination coefficient (r) was 0.996. Ninety-five percent of the DMN was degraded within the 2 hour run. Therefore, based upon the rate constant, 184 minutes would be required to degrade 99 percent of DMN.

TABLE 3. OZONE TREATMENT OF BUILDING A-1 EFFLUENT

Contact Time (min)	pH	Temp (°C)	DMN (mg/l)
	HAAP 13 Sep 0850-1050		
0	8.52	44.0	11.1
15	8.30	44.0	11.4
30	8.08	43.8	11.1
45	7.98	42.4	--
60	7.83	42.2	10.8
75	7.77	41.4	--
90	7.69	40.8	--
105	7.65	40.1	--
120	7.61	39.3	11.3

TABLE 4. ULTRAVIOLET LIGHT - OZONE TREATMENT OF BUILDING A-1 EFFLUENT

Contact Time (min)	pH	Temp (°C)	DMN (mg/l)	pH	Temp (°C)	DMN (mg/l)
	HAAP 13 Sep 1350-1550			HAAP 14 Sep 0835-1035		
0	7.80	33.0	9.8	8.52	42.2	13.0
15	7.56	32.8	6.9	8.24	42.5	--
30	7.31	32.6	5.0	8.06	43.0	7.2
45	7.18	33.0	2.9	7.87	42.5	--
60	7.11	34.0	1.8	7.75	42.2	2.8
75	7.02	34.1	1.2	7.65	41.5	--
90	6.95	34.3	0.5	7.62	41.3	--
105	6.92	34.7	0.4	7.52	41.1	--
120	--	--	0.2	--	--	0.4

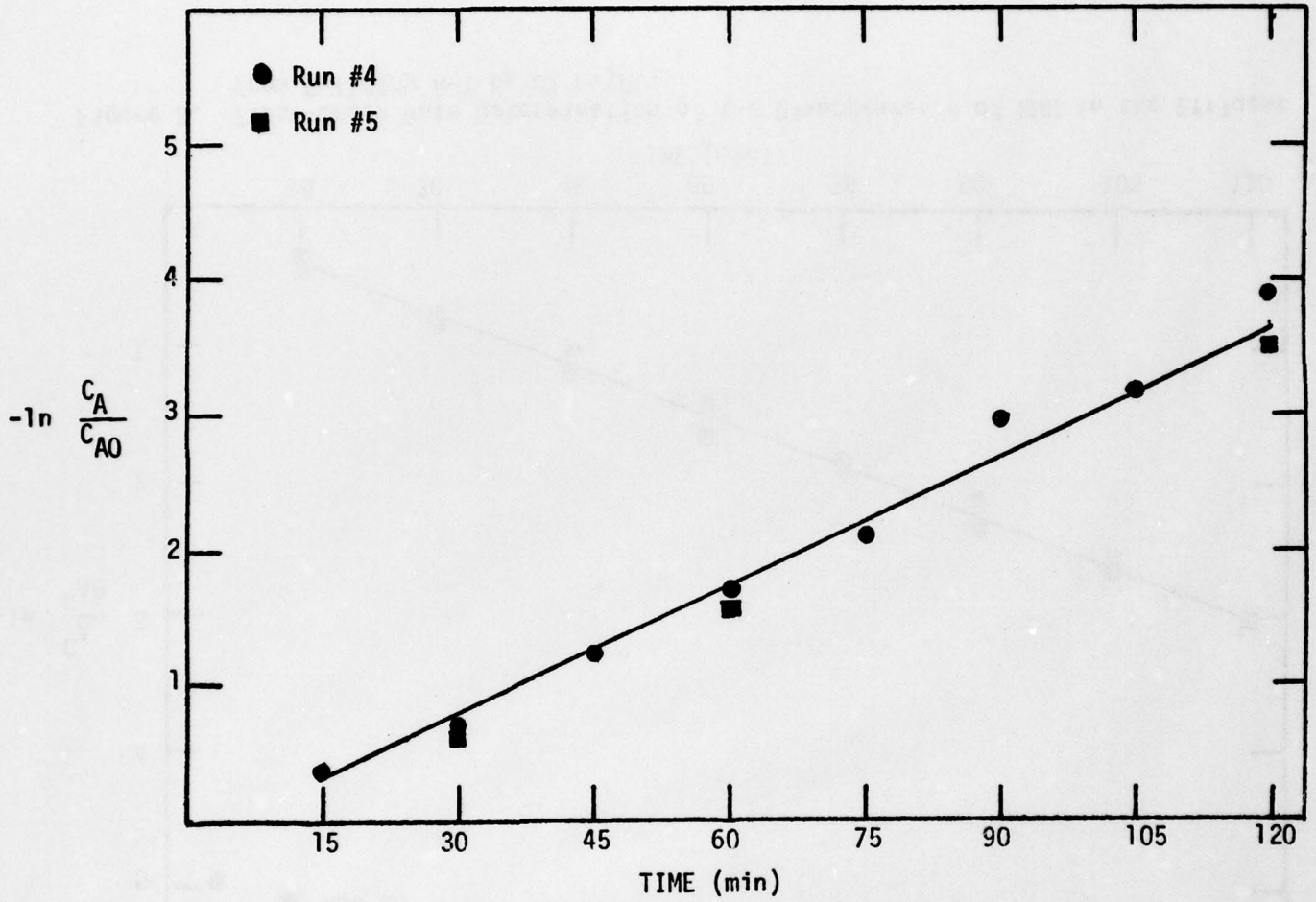


Figure 2. First-Order Rate Determination of the Disappearance of DMN in the Effluent from Building A-1 by UV-Ozone Contacting.

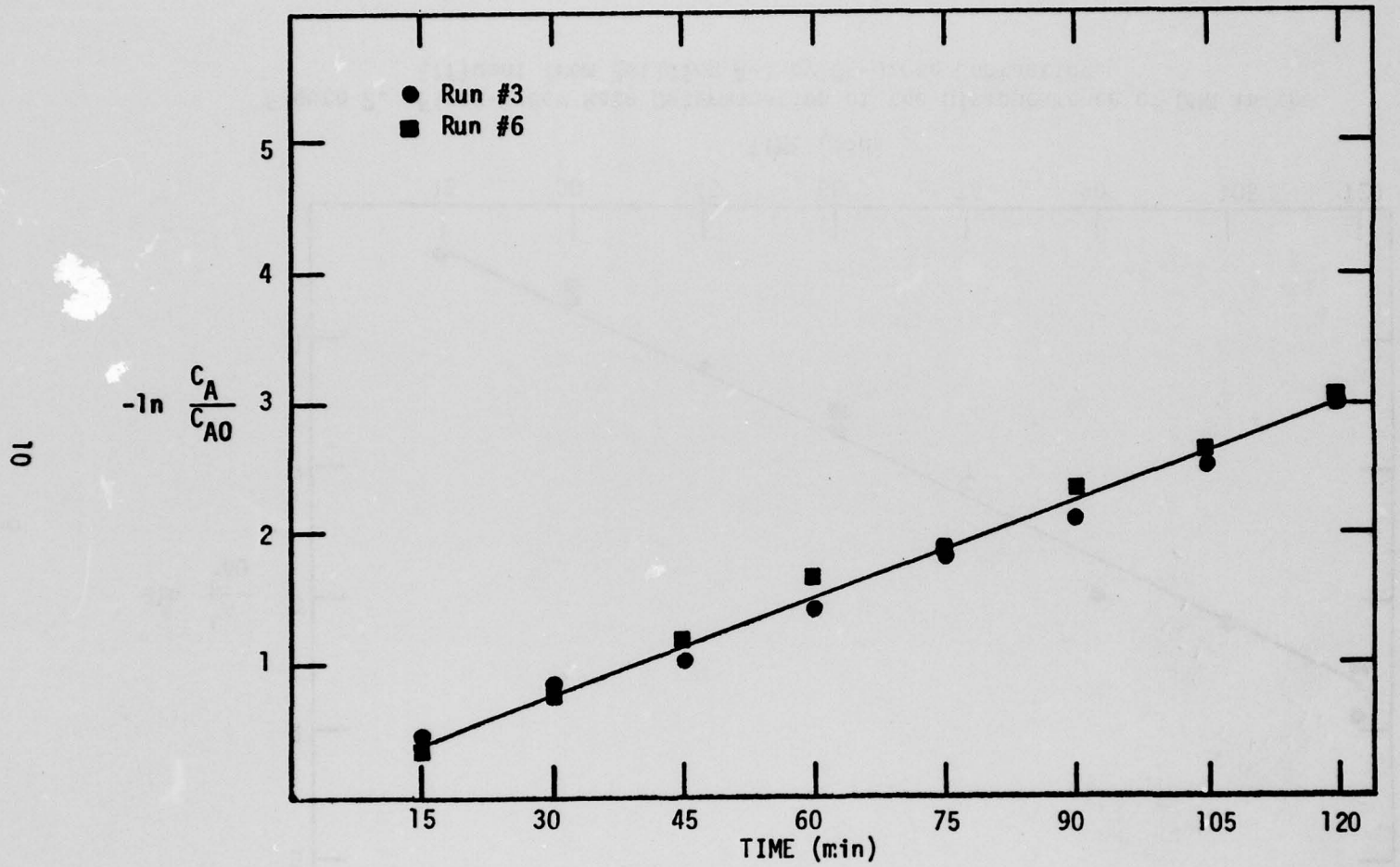


Figure 3. First-Order Rate Determination of the Disappearance of DMN in the Effluent from Building A-1 by UV Light.

TABLE 5. ULTRAVIOLET LIGHT TREATMENT OF BUILDING A-1 EFFLUENT

Contact Time (min)	pH	Temp (°C)	DMN (mg/1)	pH	Temp (°C)	DMN (mg/1)
	HAAP 13 Sep 1120-1320			HAAP 14 Sep 1100-1300		
0	8.15	44.3	10.0	8.18	44.0	13.0
15	8.22	44.0	6.4	8.17	43.8	9.5
30	8.28	43.7	4.4	8.24	43.3	6.0
45	8.26	43.0	3.6	8.26	42.9	4.0
60	8.27	42.5	2.4	8.28	41.8	2.4
75	8.25	42.4	1.6	8.30	41.6	2.0
90	8.24	41.9	1.2	8.28	41.2	1.2
105	8.21	41.6	0.8	8.20	41.4	0.9
120	8.23	41.0	0.5	8.19	41.1	0.6

Data presented in Table 6 and Figure 4 is that obtained during ultraviolet light treatment of the distillation column feedwater. This run also demonstrated first-order reduction of DMN. Using least squares, a rate constant of 0.044 min^{-1} was computed having a determination coefficient (r) of 0.993. The higher rate constant would yield 99 percent reduction of DMN after 2 hours contact time.

TABLE 6. ULTRAVIOLET LIGHT TREATMENT OF BUILDING A-1 INFLUENT

Contact Time (min)	pH	Temp (°C)	DMN (mg/l)
	HAAP 14 Sep 1340-1540		
0	12.67	26.3	9.0
15	12.64	26.7	5.7
30	12.68	27.5	2.9
45	12.69	28.6	2.3
60	12.71	29.7	1.0
75	12.74	31.0	0.4
90	12.76	32.0	0.3
105	12.77	32.8	0.1
120	12.74	33.7	0.05

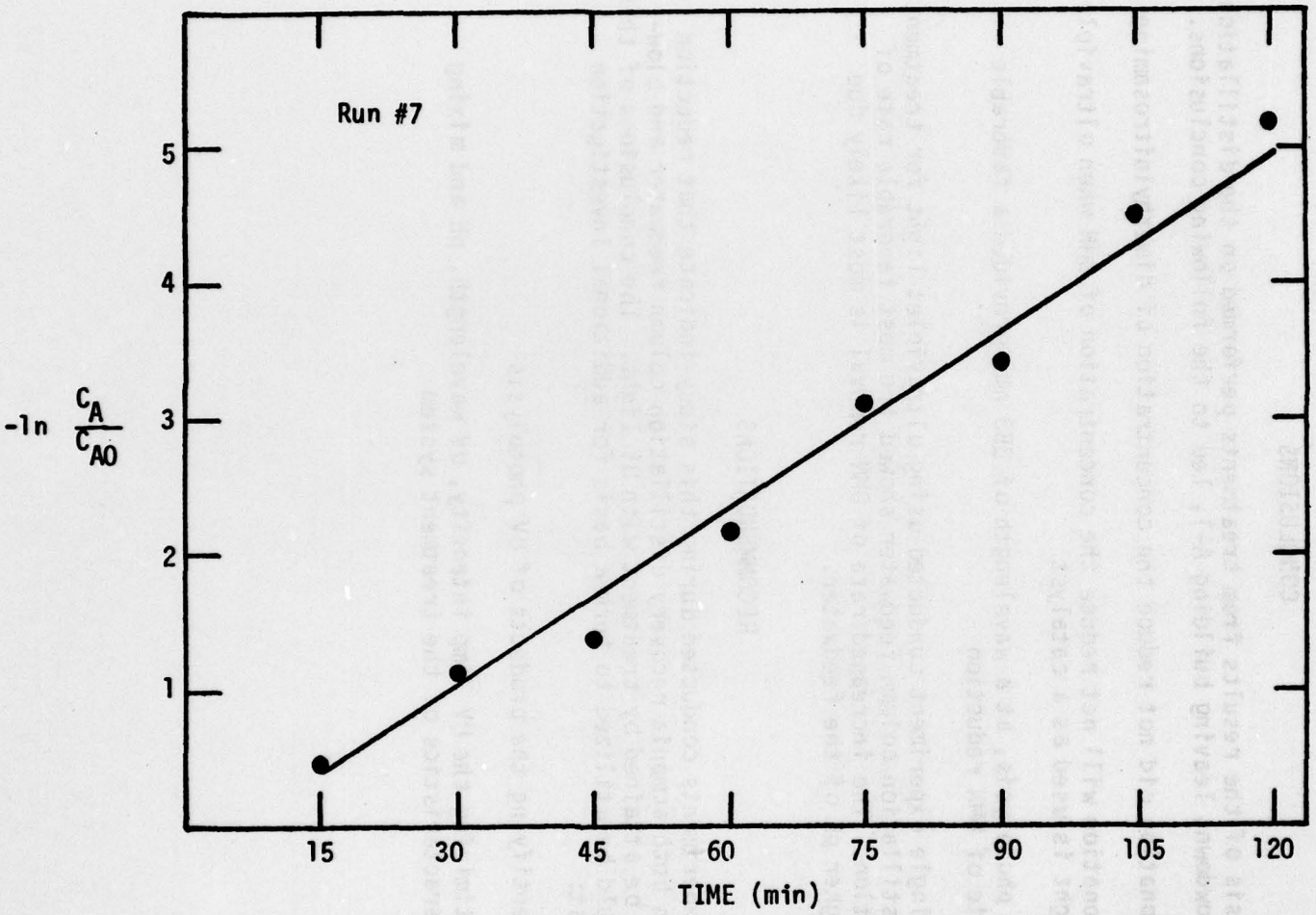


Figure 4. First-Order Rate Determination of the Disappearance of DMN in the Influent to Building A-1 by UV Light.

CONCLUSIONS

Analysis of the results from treatments performed on the distillation column blowdown, leaving building A-1, led to the following conclusions.

- Ozonation did not reduce the concentration of dimethylnitrosamine
- Ozonation will not reduce the concentration of DMN when ultraviolet light is used as a catalyst
- UV photolysis, at a wavelength of 253 nm, provided a favorable rate of DMN reduction

The single experiment conducted using ultraviolet light for treatment of the distillation column feedwater showed the most favorable rate of DMN reduction. The increased rate of DMN removal is most likely due to the higher pH of the feedwater.

RECOMMENDATIONS

The experiments conducted during this study indicate that reduction of DMN, in both ammonia recovery distillation column feedwater and blowdown, can be attained by treatment with UV light. The conclusions of this study should be utilized to form a basis for additional investigation directed at:

- Identifying the products of UV photolysis
- Optimizing the UV lamp intensity, UV wavelength, pH and mixing characteristics of the treatment system

LITERATURE CITED

1. Lee, Cheng-Chun, "Identification of Waste Products from RDX and HMX Manufacture," Contract No. DAMD-17-74-C-4073, Monthly Report No. 18, Midwest Research Institute, 425 Volker Blvd., Kansas City, MO (Jan 1979).

2. Kistner, S.L., Preliminary Report, "Water Quality Engineering Special Study No. 32-24-0180-79," US Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD.

3. Manley, T.C. and S.J. Niegowski, "Ozone," Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., Philadelphia, PA, Vol. 14, pgs 412-432.

4. McCarthy, J.J., W.F. Cowen, E.S.K. Chian and B.W. Peterman, "Evaluation of an Air Stripping-Ozone Contactor System," Technical Report 7707, US Army Medical Bioengineering Research & Development Laboratory, Ft. Detrick, Fort Detrick, Frederick, MD (1977).

5. Sierka, R.A., "Activated Carbon Treatment and Ozonation of MUST Hospital Composite and Individual Component Wastewaters," Technical Report 7202, US Army Medical Bioengineering Research & Development Laboratory, Ft. Detrick, Frederick, MD (1975) AD A008347.

6. Hewes, C.G. and R.R. Davison, "Kinetics of Ozone Decomposition and Reaction with Organics in Water," J. AIChE, 17:141 (1971).

7. Stumm, W., "Ozone as a Disinfectant for Water and Sewage," J. Boston Soc. Civ. Eng., 45(1):68 (1958).

8. Sierka, R.A. and W.F. Cowen, "The Ozone Oxidation of Hydrazine," Tyndall Air Force Base, Florida (Sep 1978).

9. De Renzo, D.J., "Unit Operation for Treatment of Hazardous Industrial Wastes," Noyes Data Corporation, Park Ridge, NJ, pp. 799-800 (1978).

10. Fotchman, E.G. and W. Eisenberg, "Treatability of Carcinogenic and Other Hazardous Organic Compounds," EPA Contract No. CI-68-03-2559, pp. 25-27 (1979).

11. Perry, F.M., E.W. Day, Jr., H.E. Magadany and D.G. Saunders, "Fate of Nitrosamines in the Environment: Photolysis in Natural Waters," Lilly Research Laboratories of Eli Lilly and Company, Indianapolis, IN.

DISTRIBUTION LIST

Project No. 3E162720A835/00/137

No. of Copies	
5	US Army Medical Research and Development Command ATTN: SGRD-AJ Fort Detrick Frederick, MD 21701
12	Defense Documentation Center ATTN: DDC-PCA Alexandria, VA 22314
1	Academy of Health Sciences, US Army ATTN: AHS-COM Fort Sam Houston, TX 78234
2	USAMBRDL Technical Library